[*Macromol. Chem. Phys.*, **202**, 1021-1030 (2001)] [Lab. of Information Processing Science]

Effect of Hydrogen Bonding on the Copolymerization of Styrene with Methacrylic Acid.

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The effects of solvents and concentration in the radical copolymerization of styrene (ST) and methacrylic acid (MAA) on the nature of the intramolecular hydrogen bonding in the prepared copolymers were investigated. The copolymerizations at lower monomer concentration in benzene gave copolymers with exceedingly higher intramolecular association ability compared to the copolymerizations in dioxane and at higher monomer concentration in benzene. This result could be explained, assuming an intrachain reaction of the end radical with MAA monomers hydrogen-bonded to MAA segments in the macroradical.

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A Regioselective Addition of Nucleophiles to Monocyclic 1,2-Thiazinylium Perchlorate: A Novel Precursor of 6-Substituted 1,2-Thiazines.

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The nucleophilic addition reactions of 4,5-diphenyl-1,2-thiazinylium perchlorate with alkoxides, silylenolates, active methylene compounds etc. regioselectively proceeded to give 6-alkoxy- and 6-alkyl-1,2-thiazines in good to high yields. The Friedel-Crafts type reaction of the perchlorate with electron-rich arenes such as 1,2,3-trimethoxy- and 1,2-dimethoxybenzenes and also with heteroaromatic compound, furan afforded the corresponding 6-aryl substituted 1,2-thiazines in moderate yields. The treatment of 6-aryl-1,2-thiazines with sulfuryl chloride-70% perchloric acid quantitatively afforded novel 4,5,6-triaryl-1,2-thiazinylium perchlolates as stable crystals.

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First Synthesis of Stable 5-Alkyl- or 4,5-Dialkyl-Substituted 1,2-Thiazinylium Salt.

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The syntheses of novel alkyl-substituted 1,2-thiazinylium salts are described. 5-Methyl- and 4,5-dimethyl-1,2-thiazinylium salts could not be isolated at room temperature because of their high moisture sensitivity . The ^{1}H NMR spectrum of the *in situ* formed products showed the characteristic protons due to the alkyl-substituted 1,2-thiazinylium salts. Moreover, treatment of the *in situ* formed 1,2-thiazinylium salts with sodium ethoxide at –30 °C gave 6-ethoxy-substituted 1,2-thiazines in low yields. These results suggest that those alkyl 1,2-thiazinilyum salts are labile to the moisture and might easily undergo polymerization *via* the deprotonation of the 4- or 5-methyl group. On the basis of the above results, we have succeeded in the first isolation of 5-*t*-butyl- and 5,8-ethano-5,8-dihydrobenzo[*d*]-1,2-thiazinylium salts as stable crystals in high yields.

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Synthesis and Thermal Transformation of Stable Monocyclic λ^4-Thiabenzenes.

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The stable monocyclic λ^4-thiabenzenes, which are stabilized with electron-withdrawing substituents such as benzoyl, cyano and alkoxycarbonyl groups, have been synthesized in high yields by proton abstraction from the corresponding thiopyranium salts with triethylamine in ethanol. The ylidic properties of the λ^4-thiabenzenes were established based on spectral and chemical evidence. Thermal decomposition of λ^4-thiabenzenes afforded alkyl-rearranged products, thienofuran derivatives (from benzoyl-substituted λ^4-thiabenzenes), and thiophene derivatives. A plausible mechanism for the formation of those products are also discussed.